

Magnetic Sensitive Thermo-induced Atomic Clusters on the Surface and into $\text{CaF}_2:\text{Eu,Ce}$ Crystals

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Abstract – The atomic clusters formed during high-temperature diffusion inside and on a surface of the crystals $\text{CaF}_2:\text{Re}$, where Re – rare-earth metals Eu, Ce, were studied. The bands at 270–280 nm and 390 nm have been observed in absorption spectra. It was established that these bands belong to the surface and near-surface centers with participation of impurity metals. By the research in a magnetic field it has been shown that magnetic atomic impurity clusters are formed in the process of the high-temperature treatment of the crystals. The structure of atomic clusters are discussed.

Investigation of the crystals and thin films which contain atomic clusters is actual because of wide prospects of their application in the field of nanotechnologies. Earlier the research of atomic clusters in the surface films formed due to the high-temperature impurity diffusion has been studied in crystals $\text{LiF}:\text{Ni}$, Co [1].

The clusters formed during of high-temperature impurity diffusion inside and on a surface of crystals $\text{CaF}_2:\text{Re}^{3+}$ (Re: Eu, Ce) were studied. The crystals have been grown up by Stockbarger method in graphite crucibles in vacuum. The rare-earth metal impurities were entered into crystals by addition of suitable salts of the fluorides in the melt.

The crystals have been annealed in laboratory furnace Snol in a temperature interval from 473 K to 1023 K in vacuum $10^{-4} - 10^{-5}$ Torr or in the air. The temperature was established with speed of heating (and also cooling) to 150 K/h, and supported at the set level with exact ± 5 K. After high temperature annealing crystals were cooled up to 573 K and then taken out from the furnace on air. Optical absorption spectra in UV, visible and IR regions were measured using spectrophotometers Carl Zeiss Specord UV VIS and IFS 25. The study of the surface structure and the analysis of impurity content in the films were carried out using X-Ray electron-probe microanalyser "Superprobe-733" (Jeol, Japan). The measurements were fulfilled under an accelerating voltage 20 kV; sample current of 20 nA, electron beam diameter of 1 μm and counting time of 40 s. The crystal surface was covered by a conductive carbon layer (thick ~ 25 nm). The referent samples $\text{LiEu}(\text{MoO}_4)_2$ and $\text{LiCe}(\text{WO}_4)_2$ were used as comparative ones. The different points on the surface were examined before and after annealing of the

crystals. The study of magnetic properties of the films was carried out by the method of rotational moments using the rotary anisometer with $B = 1$ T. The concentration of impurities Eu and Ce were in the ranges 0.6 – 2.2 w.% and 0.01 – 0.1 w.%, respectively.

The absorption spectra of CaF_2 (0.6 w.% Eu, 0.1 w.% Ce) were measured before and after annealing at various conditions (Fig. 1). The thermo-treatment has not significant effect on the spectra of crystals annealed at 673 K and 773 K. In crystals annealed at 823 K and 873 K in the air the surface films are observed visually and exhibited in absorption spectra. With increase in time of annealing the edge of a absorption band at 200 nm rises and on its slope a band at 390 nm and wide band 270–280 nm are increased (Fig. 1, curve 2). The indicated bands are more intensive in a crystals annealed at 873 K. The band of valence vibration of OH^- ions in CaF_2 (3640 cm^{-1} [2]) in IR spectrum is not observed. As a result of an annealing at 1073 K a more dense films are formed, an optical density over all spectrum is $D \geq 1.0$, and the edge of a band at 200 nm is shifted to 300 nm. In this spectrum the band about 270–280 nm (Fig. 1, curve 3) is observed. Measurement of IR spectra of crystals show presence of OH^- ions in crystals annealed at 1073 K in the air. In case

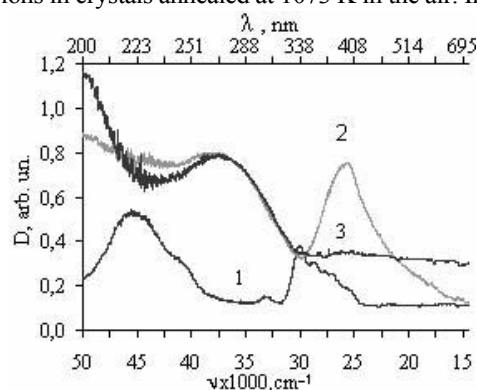


Fig. 1. Absorption spectra of $\text{CaF}_2:\text{Eu}:\text{Ce}$: 1 – before annealing, 2 – after 10h annealing in air at 873 K, 3 – after 2h annealing in the air at 1073 K

of annealing in the vacuum any absorption bands in UV, visible and IR regions are not observed.

It was found that after the thermo-treatment the crystals display magnetic properties. The measurements of the magnetic sensitivity were carried out using the method of definition of a corner of turn α of string with the sample in a magnetic field. The Table 1 shows that

magnetic sensitivity is caused by internal crystal defects as it is observed also in annealed crystals which previously polishing. (The thickness of a crystals due to polishing decreased by 0.05 – 0.1 mm). In crystals annealed at high temperature (1073 K) the magnetic sensitivity is the maximum. Magnetic properties are observed in the crystals annealed in the air as well as in the vacuum.

It is known that at $T \geq 823$ K in CaF_2 diffuse oxygen from a surrounding atmosphere [2]. It is fixed in a

spectrum on edge nearby 200 nm though the edge of a band rises and due to formation of a surface film. As it is followed from our results at these temperatures active dissociation of water molecules on a surface and OH^- ions migration inside a crystal do not occur. At annealing temperature 1073 K OH^- ions are appeared in sites of a lattice crystal, possibly, as a result of reaction:

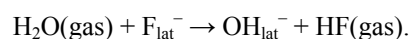


Table 1. Specific magnetic sensitivity (α , mm) of $\text{CaF}_2:\text{Eu}$ crystals annealed at different conditions

Sample (surface)	Duration of annealing, hour	Temperature of annealing, K	Annealing medium	Magnetic sensitivity by an unit volume of the crystal
1 (non-polished)	10	773	air	0.30
2 (non-polished)	10	823	air	0.60
3 (polished)	10	873	air	0.71
4 (polished)	10	1073	air	6.20
5 (polished)	6	1073	air	3.06
6 (non-polished)	2	1073	vacuum 10^{-4} – 10^{-5} Torr	0.48
7 (non-polished)	2	1073	vacuum 10^{-4} – 10^{-5} Torr	1.05
8 (polished)	2	1073	vacuum 10^{-4} – 10^{-5} Torr	1.12

Then OH^- ions migrate in a crystal lattice by the mechanism anion migrations to a impurity-interstitial complexes $n(\text{Re}_c^{3+}-\text{F}_i^-)$ where it is not stable. Molecule HF leaves through HF_2^- anion to crystal surface, and Re_c^{3+} complexes with O^- anions are formed. Thus, in our crystals two kinds of atomic clusters can be created. The first type consists of Re^{3+} ions (in particular, Eu,Ce), replacing Ca^{2+} ions, compensating interstitial F_i^- ions and displaced from sites F_a^- ions. The second type consists of Re^{3+} ions, replacing Ca^{2+} ions, and O^- ions in anion sites. The quantity of Eu^{3+} ions in such clusters can reach six or more. These clusters also can be carriers of magnetic properties of annealed crystals.

Earlier two types of clusters in CaF_2 was observed by ESR method [3]. Existence of atomic clusters proves to be true researches of authors [4] where it is shown that Re^{3+} impurities in the CaF_2 crystals are not distributed in a crystal in regular intervals, replacing statistically atoms of calcium, and form nanoscale clusters of the certain atomic structure which managed to be defined by means of methods of neutron- and x-ray structure analysis. Moreover, Re^{3+} ions in CaF_2 form clusters of different structure.

Occurrence of magnetic properties of atomic clusters in our crystals is in agreement with the results represented in work [5]. This author informs on origin small-atomic magnetic-sensitive clusters in the crystals $\text{NaCl}:\text{Eu}$. Accordingly [5], the magnetic-sensitive clusters are dimers of impurity-vacancy dipoles of europium (pair dipoles) in which backs are connected by exchange interaction and are focused in parallel each other.

In the process of thermo-diffusion at $T \geq 823$ K the films on the surface of $\text{CaF}_2:\text{Re}^{3+}$ crystals are formed. Disappearance of the band at 390 nm in absorption spectra after polishing a surface of a crystal

testifies about surface and near-surface nature of the centers, its forming. Reduction of intensity of a band at 270–280 nm band from 2 up to 10 times at polishing testifies to its accessory to the centers which are being in at-surface area of a crystal, mainly.

Into structure of the surface centers enters activator as bands at 390 nm and 270–280 nm are absent in spectra of a pure crystal. The surface centers consist also of products of physical and chemical reactions with participation of atmospheric gases, such as O_2 , CO_2 , H_2O and etc. It proves to be true that, first, $T > 850$ K actively there is a decomposition of water at a surface of a crystal and OH^- ions are formed and diffused into the crystal. Secondly, at $T > 850$ K there is a diffusion of an oxygen impurity in a crystal. Formed products participate in physical and chemical reactions. Absence of films at annealing of crystals in vacuum testifies to formation oxides, hydroxides and oxygen fluorides of Re^{3+} metals on a surface of crystals, annealed on the air. The analysis of magnetic properties of crystals $\text{CaF}_2:\text{Eu,Ce}$ after polishing has shown, that the surface centers do not have magnetic properties at a room temperature, unlike studied by us before crystals $\text{LiF}:\text{Ni}$ [1].

References

- [1] L.I. Bryukvina, E.A.Ermolaeva, S.N.Pidgursky, L.Ph. Suvorova, V.M. Khulugurov, FTT, **48**, 64 (2006).
- [2] W. Bollman, Phys.stat.sol. (a). **57**, 601 (1960).
- [3] C. R.A. Catlow, J. Phys. Chem. Sol. **38**, 1131 (1977).
- [4] V.P. Sobolev, *The Earth Trifluorides. Part 2, Introduction to Materials Science of Multicomponent Metal Fluoride Crystals*, Barcelona, Institut d'Estudis Catalans, 2001, p. 905.
- [5] R.P. Morgunov, Ukr.Fiz.Zhurn. **174**, 131 (2004).